APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 5, 117-124 (1991)

Determination of arsenic and arsenic compounds in natural gas samples

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Organic arsenic compounds (trialkylarsines) present in natural gas were extracted by 10 cm^3 of concentrated nitric acid from 1 dm^3 of gas kept at ambient pressure and temperature. The flask containing the gas and the acid was shaken for 1 h on a platform shaker set at the highest speed. The resulting solution was mixed with concentrated sulfuric acid and heated to convert all arsenic compounds to arsenate. Total arsenic was determined in the mineralized solutions by hydride generation. The arsenic concentrations in natural gas samples from a number of wells in several gas fields were in the range 0.01–63 µg As dm^{-3}. Replicate determinations of arsenic in a gas sample with an arsenic concentration of 5.9 µg dm^{-3} had a relative standard deviation of 1.7%. Because of the high blank values, the lowest arsenic concentration that could be reliably determined was 5 ng As dm^{-3} gas. Analysis of nonmineralized extracts by hydride generation identified trimethylarsine as the major arsenic compound in natural gas. Low-temperature gas chromatography–mass spectrometry showed more directly than the hydride generation technique, that trimethylarsine accounts for 55–80% of the total arsenic in several gas samples. Dimethylethylarsine, methyldiethylarsine, and triethylarsine were also identified, in concentrations decreasing with increasing molecular mass of the arsines.

Keywords: Natural gas, arsenic, trimethylarsine, dimethyethylarsine, methyldiethylarsine, triethylarsine, extraction, nitric acid, analysis

INTRODUCTION

Arsenic is the 20th most abundant element in the earth's crust, with an average concentration of a few milligrams of arsenic per kilogram. Arsenic is ubiquitous. The arsenic concentration in seawater, at 2 µg As dm^{-3}, is one of the lowest among common environmental materials. Arsenic is not only present in inorganic materials such as water, rocks and soils, but also in organisms—particularly in marine organisms—and in crude petroleum.[1-4] Because living marine organisms are known to accumulate arsenic efficiently to concentrations several thousand times above the ambient concentration in seawater, organisms that lived millions of years ago very likely had the same capability. These arsenic-rich organisms were converted to petroleum and probably are the source of the arsenic now found in crude petroleum. The transformation of biological materials to petroleum is accompanied by the formation of hydrocarbon gases with methane as the major component. The biogenic arsenic compounds in marine organisms are methylated arsenic derivatives, many of which have three methyl groups bonded to the arsenic atom. An example of such a compound is arsenobetaine $[(CH_3)_3\overset{+}{As}CH_2CO\bar{O}^-]$, the carboxymethyl(trimethyl)arsonium zwitterion. This compound is very likely decarboxylated at elevated temperatures. The resultant tetramethylarsonium salt can be demethylated. Trimethylarsine, the product of this reaction, should dissolve in the liquid petroleum and partition into the gas phase. According to this hypothesis, trimethylarsine should be present in natural gas. A search of the literature revealed that very little information about arsenic in hydrocarbon gases exists.[5] The experiments reported here were carried out to establish the presence of arsenic in natural gas, to develop a

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0268-2605/91/020117-08$05.00

Received 19 October 1990
Accepted 31 December 1990

method for the routine determination of arsenic in this matrix, and to identify the arsenic compounds.

EXPERIMENTAL

Sample collection, instrumentation and reagents

Natural gas was collected in the field in aluminium or iron bombs at the pressures in the pipeline. The bombs were equipped with valves, to which a Teflon hose could be connected. A 1-dm^3 round-bottomed flask with a center 24/40 ground-glass neck and a side arm with a Teflon stopcock was completely filled with water. The water was emptied into a graduated cylinder to determine the exact volume of the flask. The flask was then dried.

A standard solution of arsenate (1000 mg As dm^{-3}) was prepared from Merck & Co. reagent-grade sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$) and distilled, deionized water. The dilute standard solution (1 mg As dm^{-3}) was prepared fresh daily. A 2% (w/v) solution of sodium tetrahydroborate in 0.1 mol dm^{-3} aqueous sodium hydroxide was prepared from the reagent-grade powder (Aldrich). The solution was filtered through a Whatman No. 1 filter paper. This solution was found to be stable for at least four days. Concentrated (15 mol dm^{-3}) reagent-grade nitric acid was used for the extraction of the arsenic compounds from the gas. All other chemicals used were of analytical grade or better. All glassware was rinsed with dilute nitric acid, washed with distilled water, rinsed with deionized water, and then dried. A Lab-Line Junior Orbit Shaker with platform (Lab-Line Instruments Inc., Melrose Park, Illinois) and adjustable speed was used to agitate the nitric acid/gas mixtures. The hydride generation system consisted of a reduction chamber, a trap cooled by dry ice/isopropanol to freeze out water from the gas stream, a trap cooled by liquid nitrogen to collect the arsines, and a dc helium plasma to atomize the arsines and excite the arsenic atoms. The 228.7 nm emission of arsenic was monitored.[6,7] A Hewlett–Packard 5970 MSD mass spectrometer connected to a Hewlett–Packard 5890 gas chromatograph and a Hewlett–Packard 59970 MS Chem Station computer system was used for the GC MS experiments with the standard arsines and the natural gas samples.

Extraction of arsenic compounds from natural gas collected in bombs

The stoppered 1-dm^3 flask with side arm was evacuated with an oil vacuum pump for 30 min. The bomb containing a natural gas sample was connected to the side arm of the flask with a piece of thick-walled Teflon tubing. The valve on the bomb and the Teflon stopcock were carefully opened, allowing the gas to fill the flask to a pressure slightly above the barometric pressure. To prevent the stopper from being blown from the flask, the stopper was held in the neck by springs or by hand. When the flask had been filled with the gas, the valve on the bomb and the stopcock on the sidearm were closed. A 25-cm^3 dropping funnel without pressure-equalizing arm was charged with 10 cm^3 of 15 mol dm^{-3} nitric acid. The stopper on the flask was quickly replaced by the dropping funnel. During this process the gas pressure inside the flask equalized to atmospheric pressure. The nitric acid was transferred into the flask. When all the nitric acid had dropped into the flask, the stopcock of the dropping funnel was closed. The dropping funnel was quickly removed and replaced by a lightly greased ground-glass stopper. The stopper was secured by springs or clamps. The flask was then securely clamped to the shaker and shaken for at least 30 min at the highest setting. The liquid in the flask was poured into a 250-cm^3 volumetric flask. The extraction flask was rinsed several times with 5-cm^3 portions of distilled water. The wash water was also transferred into the volumetric flask. The volumetric flask was filled to the mark with distilled water and shaken to homogenize the solution.

Dependence of the extraction efficiency on shaking speed, shaking time, volume of nitric acid and nitric acid concentration

Extraction experiments were performed as described above. For each series gas from the same bomb was taken. One variable was changed at a time in the sequence shaking time, volume of concentrated nitric acid, concentration of nitric acid. The optimal condition for the first variable was used to investigate the effect of the second variable and the optimal condition for the first and second variables to study the effect of the third.

Extraction of arsenic compounds in the field

The valve providing access to the natural gas in the pipeline was opened. A vigorous stream of gas was allowed to escape through the valve to clean the passage and blow out any solid deposits. The ground-glass stopper was removed from the 1-dm^3 flask, the stopcock on the sidearm was opened, and the sidearm was connected to the valve on the pipeline with a piece of Teflon tubing. A stream of gas was passed through the flask for several minutes. When all the air in the flask had been replaced by the natural gas, the lightly greased ground-glass stopper was pushed into the neck at the same time at which the valve on the pipeline was closed. After the pipeline valve had been closed, the stopcock on the sidearm was also closed. This procedure assures that the gas pressure in the flask is slightly higher than atmospheric pressure. The arsenic compounds were then extracted from the gas sample as described for the experiments with gas collected in bombs.

Determination of arsenic compounds in the extracts by hydride generation

Aliquots of the diluted extracts were transferred to the reduction vessel of the hydride generation system. The volumes of the aliquots are determined by the concentration of the arsenic compounds in the solutions and may range from microliters to milliliters. A 0.5 mol dm^{-3} phosphate buffer solution of pH 6.5 (10 cm^3) was added and the total volume in the reduction vessel brought to 20 cm^3 with distilled water. Only arsenite (AsO_3^{3-}) is reduced to arsine at this pH by sodium borohydride. To another aliquot an aqueous solution of oxalic acid (5% (w/v), 10 cm^3) was added and the total volume in the reduction vessel again brought to 20 cm^3 with distilled water. At this pH arsenite and arsenate (AsO_4^{3-}) are reduced to arsine, and mono-, di- and tri-methylated pentavalent arsenic compounds to the corresponding arsines. The arsines were condensed in a liquid nitrogen trap and subsequently volatilized into the dc-helium plasma. The arsenic emission at 228.7 nm was monitored. The arsines were identified by their retention times. Arsenite, arsenate, methylarsonic acid [$CH_3AsO(OH)_2$] dimethylarsinic acid [$(CH_3)_2AsO\,OH$] and trimethylarsine oxide [$(CH_3)_3AsO$] served as reference materials.[6,7]

Determination of total arsenic in the extracts

For the determination of total arsenic, an aliquot of an extract was placed in a 250-cm^3 beaker. Nitric acid (15 mol dm^{-3}, 30 cm^3) and sulfuric acid (18 mol dm^{-3}, 15 cm^3) were carefully added. After a few glass beads (6 mm diameter) had been added, the beaker was covered with a watchglass and heated on a hot plate to keep the solution gently boiling for 1 h. When white fumes of sulfur trioxide [SO_3] appeared, the solution was cooled to room temperature. The cool solution was carefully diluted with distilled water and heated again, until white fumes appeared. The solution was cooled to room temperature and transferred to a 50-cm^3 volumetric flask. The beaker was rinsed with several small portions of distilled water. The washings were poured into the volumetric flask. The flask was filled to the mark with distilled water and then shaken to homogenize the solution. Aliquots of this solution that contain arsenate as the only arsenic compound were transferred into the reduction vessel of the hydride generation system. The arsenate was reduced at pH 1 with sodium borohydride and the generated arsine passed into the dc-helium plasma as described.[6,7]

Identification of arsenic compounds by gas chromatography–mass spectrometry

An aliquot (20 cm^{-3} at atmosphere pressure) of the gas sample collected in bombs was introduced over a period of 20 min into a 30-m, 0.25-mm i.d. HP-1 fused-silica capillary column cooled to 0°C. During this time the column was held at 0°C. When the entire sample was in the column, the column oven was programmed to increase the temperature by 4°C min^{-1} until a temperature of 290°C had been reached. The column was kept at this temperature for 35 min. Helium at a flow rate of 1 cm^3 min^{-1} was used as the carrier gas.

For the identification of the arsenic compounds and the determination of their concentrations, the mass spectrometer was operated in the selected-ion-monitoring mode or the selected-ion-chromatogram-reconstruction mode. The full

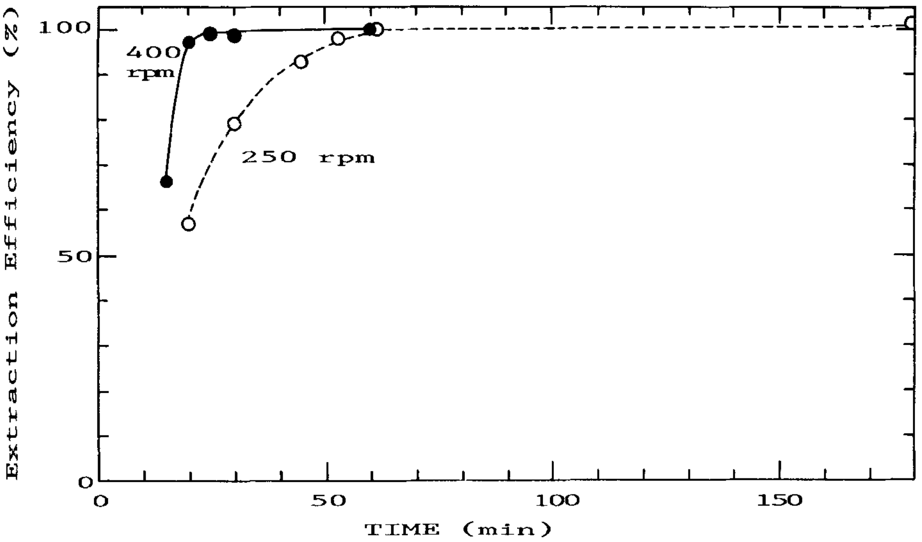

Figure 1 The influence of shaking speed and shaking time on the efficiency of the extraction of arsenic compounds from natural gas into concentrated nitric acid.

mass range (35–450 m/z) was scanned every 1.2 s to obtain the mass spectra of the column effluent. The chromatograms were reconstructed for each arsenic compound by plotting the intensity of the peaks of selected ions versus time. Each compound was then identified by the specific ion response and the retention time. The concentration of each compound was determined from the areas of the reconstructed chromatographic peaks belonging to molecular or fragment ions. Synthetic samples of trimethylarsine, dimethylethylarsine, methyldiethylarsine, and triethylarsine were introduced into the GCMS under the conditions described for the natural gas samples to determine retention times and the mass spectrometric behavior of these standards, and identify the signals in the mass spectra most suitable for selected-ion monitoring.

RESULTS AND DISCUSSION

Arsenic can be determined by a variety of methods based on colorimetry, electrochemical reduction, atomic emission spectrometry and atomic absorption spectrometry. Most of these methods require that the analyte be present in an aqueous matrix. The presence of arsenic compounds in natural gas necessitated the development of a procedure that allows the determination of total arsenic in natural gas samples at concentrations approaching a few nanograms of arsenic per liter of gas. Although a direct determination of arsenic in the gas without treating the sample is desirable and feasible, the cost and scarcity of the required instrumentation (low-temperature gas chromatograph coupled to a high-resolution mass spectrometer) led to the decision to find ways to extract the arsenic compounds quantitatively from the gas into an aqueous matrix, in which arsenic and arsenic compounds can be determined by the hydride generation technique. The hydride generation technique is known to have the low detection limits needed. Preliminary experiments indicated that nitric acid is capable of extracting arsenic compounds from natural gas. Therefore, concentrated (15 mol dm^{-3}) nitric acid was investigated in detail as the extracting reagent.

Effects of shaking speed and time

A natural gas sample containing arsenic was shaken in a 1-dm^3 flask with 10 cm^3 of concentrated nitric acid at the maximal shaker speed (400 rpm) and at 250 rpm for periods varying from 15 min to 3 h. The extracts were mineralized. Total arsenic was determined in the mineralized solutions buffered with oxalic acid to approximately pH 1 by the hydride generation technique. The shortest time at which quantitative extraction of the arsenic from the natural gas is possible depends on the shaking speed. At 400 rpm this time is 30 min, at 250 rpm 60 min (Fig. 1). At longer shaking times the experimental arsenic concentrations were independent of the shaking time. An arsenic concentration of $6.06 \pm 0.06\,\mu g\,dm^{-3}$ was found in the gas sample used for this study. All other experiments were carried out with a shaking time of 1 h. The dependence of the extraction efficiency on the shaking speed for the 1-h shaking time was investigated. Under these conditions all the arsenic is transferred from the gas to the concentrated nitric acid at shaking speeds higher than 125 rpm. Without any agitation of the flask, approximately 60% of the arsenic in the gas was found in the nitric acid after 1-h contact between the phases (Fig. 2). The dependence of the extraction efficiency on shaker speed and shaking time should be investigated, before a shaker is used for the extraction of arsenic compounds from natural gas samples.

Effect of the volume of nitric acid

Extractions were carried out under standard conditions ($1\,dm^3$ gas, 1 h shaking time) using 5, 10, 15, or $20\,cm^3$ concentrated nitric acid. In all these experiments the same arsenic concentration of $6.0 \pm 0.1\,\mu g\,As\,dm^{-3}$, independent of the nitric acid volume, was found. All further experiments were carried out with $10\,cm^3$ of concentrated nitric acid.

Effect of nitric acid concentration

Natural gas samples were extracted for 1 h at maximal shaking speed with $10\,cm^3$ of $1\,mol\,dm^{-3}$, $5.0\,mol\,dm^{-3}$, or concentrated nitric acid. The extracts were mineralized and total arsenic determined by hydride generation. The experiment with concentrated nitric acid yielded an arsenic concentration of $0.74\,\mu g\,dm^{-3}$. With $5\,mol\,dm^{-3}$ nitric acid only 91% of the arsenic were extracted, with $1\,mol\,dm^{-3}$ nitric acid only 47%. These data suggest that nitric acid does not have to be concentrated for the quantitative extraction of arsenic compounds from natural gas. However, concentrated nitric acid was employed for routine extractions to avoid the dilution step as a source of potential contamination.

Determination of total arsenic in natural gas

A large number of natural gas samples were extracted with $10\,cm^3$ of concentrated nitric acid for 1 h at the highest shaker speed, mineralized with a boiling mixture of concentrated nitric and concentrated sulfuric acids, the mineralized solutions diluted, and total arsenic determined in these solutions by the hydride generation technique. Because all arsenic in these solutions is present as arsenate, only arsine (AsH_3) is formed. The calibration curve constructed using the peak heights of the signals was linear in the range 10–70 ng arsenic. The total volume of the solution in the reduction vessel was kept at $20\,cm^3$. Under these conditions a gas sample was analyzed six times. The arsenic concentration was found to be $5.9 \pm 0.1\,\mu g\,As\,dm^{-3}$ (relative standard deviation

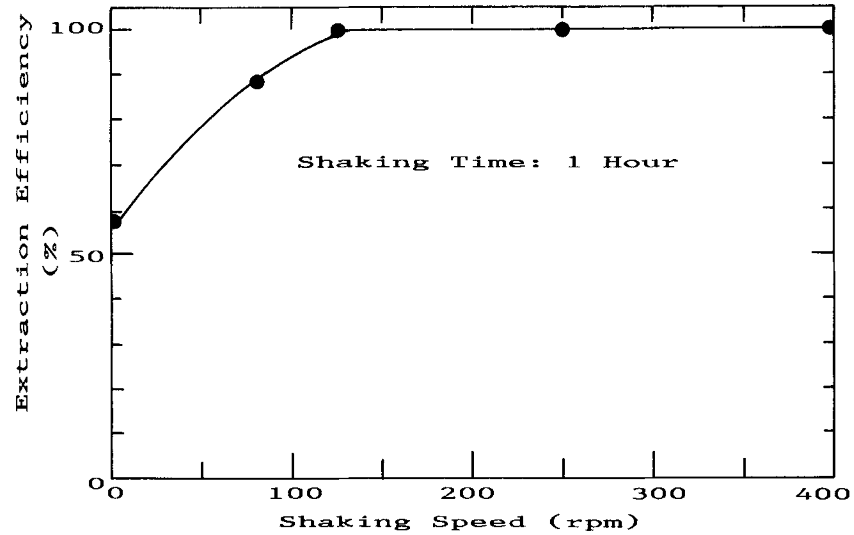

Figure 2 The influence of the shaking speed on the efficiency of the extraction of arsenic compounds from natural gas into concentrated nitric acid for a shaking time of 1 h.

1.7%). The arsenic concentrations in natural gas samples from a number of wells in several gas fields ranged from 0.01 to 63.0 μg As dm^{-3}. These concentrations may not be accurate, because the samples were collected in bombs made from aluminium, iron, or steel that may remove arsenic from the gas by sorption onto the walls of the bomb. Experiments with gas samples collected from the same well at the same time in glass flasks and in 304 stainless-steel bombs indicated that the arsenic concentrations in gas samples collected in the stainless-steel bombs were up to two orders of magnitude lower than the concentrations in corresponding gas samples collected in glass flasks. The container materials that are suitable for collecting arsenic-containing gases have not yet been identified. The results may also be inaccurate, because the extraction may not be complete or it may be complete only for certain types of arsenic compounds present in the gas. Unfortunately, standard natural gas samples with concentrations of total arsenic or certain arsenic compounds that are certified are not available. However, the precision of the results from repeated analyses under a variety of conditions of less than 5% relative standard deviation indicates that all of the arsenic is extracted from the gas.

With every set of analyses, blanks were processed. The blanks were found to be in the region of 10 ng As dm^{-3} and represent the contributions of arsenic from the reagents, the containers and the laboratory environment. Because much work of a synthetic and analytical nature with respect to arsenic compounds is carried out in the laboratories, the major contribution of arsenic to the blank comes from the laboratory contaminated with arsenic compounds. Although the detection limit of the hydride generation system is 1 ng arsenic or less, the high blank values allow only arsenic concentrations of 5 ng dm^{-3} or higher to be determined with acceptable precision. All concentrations refer to the volume of gas equal to the volume of the flask in which the extraction is carried out at ambient pressure and temperature. The gas volume was not corrected for the volume occupied by the 10 cm^3 of nitric acid.

Identification of arsenic compounds in natural gas by hydride generation

When the solutions obtained by extraction of natural gas with concentrated nitric acid were reduced immediately with sodium borohydride at approximately pH 1, the reduction products condensed in a trap cooled with liquid nitrogen, and the arsine(s) then volatilized into the helium plasma, trimethylarsine was identified as the only arsenic compound. However, when the extracts were allowed to stand at room temperature for extended periods, dimethylarsine, methylarsine and arsine were identified. The intensity of the trimethylarsine signal decreased and the signals for the other arsines increased with the length of the period between extraction and reduction. These results suggest that at least one of the arsenic compounds in the gas is an arsenic derivative with three methyl groups bonded to the arsenic atom. Although the hydride generation technique does not distinguish between trivalent and pentavalent methylated arsenic compounds, the arsenic compound in the gas must be trimethylarsine. Trimethylarsine oxide, on chemical grounds a possible precursor of the detected trimethylarsine, is a solid and therefore it is unlikely to be present in the gas phase at room temperature. Trimethylarsine sulfide, identified as a solid deposit in natural gas pipelines (K. J. Irgolic, unpublished data) is not reducible by sodium borohydride and therefore cannot be the source of the trimethylarsine found by hydride generation. Comparison of the arsenic concentration in the gas based on trimethylarsine and the arsenic concentration found by reduction of the mineralized extracts indicated that trimethylarsine can account only for approximately half of the arsenic in the gas. The other arsenic compounds are very likely tertiary methylethylarsines. Among inorganic arsenic compounds only AsH_3 could be present in the gas. Arsine is a rather unstable compound that would have been oxidized to arsenate during the extraction of the gas with nitric acid. Arsenate would have been reduced to arsine by sodium borohydride. No arsine was found in the fresh extracts. Therefore, arsine cannot be present in the gas samples investigated. Incidentally the helium stream could not transport ethylarsines to the detector for volatility reasons.

Identification of arsenic compounds in natural gas by GC MS

Low-temperature GC MS made it possible to directly identify arsenic compounds in natural gas samples that had been collected in stainless-steel bombs. The 30-m capillary column was held at 0°C while the 20-cm^3 sample of natural gas was

Table 1 Formulae, molecular masses, retention times, and *m/z* values for mass-spectral signals most suitable for selected-ion monitoring for trialkylarsines

Arsine	Molecular mass	Retention time (min)	*m/z*	
			M^+	Fragment
$(CH_3)_3As$	120	48.5	120	105 $(M-CH_3)$
$(CH_3)_3AsC_2H_5$	134	51.3	134	119 $(M-CH_3)$
$CH_3As(C_2H_5)_2$	148	52.8	148	120 $(M-C_2H_4)$
$As(C_2H_5)_3$	162	54.3	162	105 $(M-C_2H_4-C_2H_5)$

loaded onto the column. The column is severely overloaded with hdyrocarbons from this procedure. Mass spectra were recorded while the column temperature was raised to 290°C at 4°C min^{-1} and kept at 200°C for 35 min. Selected-ion monitoring and selected-ion chromatogram reconstruction allowed the identification of the arsenic compounds. The retention times for the arsine standards (trimethylarsine, dimethylethylarsine, methyldiethylarsine, triethylarsine) under these conditions and the mass-spectral signals most useful for selected-ion monitoring are listed in Table 1.

Gas samples from four wells were analyzed. All four arsenic compounds were found in two samples and they are probably present in all of the samples but at concentrations below the detection limits of the GC MS system used. The results are summarized in Table 2. Trimethylarsine accounts for 55–80% of the arsenic found in natural gas by the nitric acid extraction/mineralization/hydride generation method; another 5–10% are contributed by methylethylarsines and triethylarsine. Thus, the four trialkylarsines in Table 2 make up 55–89% of the total arsenic. The incomplete arsenic balance suggests that other arsenic compounds, probably higher-molecular-mass trialkylarsines, are present in the gas. Trimethylarsine oxide and trimethylarsine sulfide did not elute from the GC column under the conditions employed for the analysis of the gas samples.

Table 2 Concentrations of trialkylarsines in natural gas by GC MS and concentrations of total arsenic by hydride generation

Arsine	Arsenic (ng As dm^{-3})[b]			
	Well 1	Well 2	Well 3	Well 4
$(CH_3)_3As$	40(64)[a]	21(34)[a]	103(165)[a]	202(324)[a]
$(CH_3)_3As \cdot C_2H_5$	1(2)[a]	<	7(12)[a]	11(19)[a]
$CH_3As(C_2H_5)_2$	0.5(1)[a]	<	5(9)[a]	3(7)[a]
$As(C_2H_5)_3$	<	<	1.4(3)[a]	1(2)[a]
Total As by HG	55	38	130	270
Total As by GC MS	41.5	21	116	217

[a] Values in parentheses are concentrations in terms of ng arsenic compound per dm^3 gas.

[b] The detection limit of the GC MS system is approximately 0.5 ng of trimethylarsine; <: below detection limit.

CONCLUSIONS

Total arsenic can be determined in natural gas precisely and probably accurately by extracting one-liter gas samples with 10 cm^3 concentrated nitric acid by vigorous shaking for 1 h on a shaker, mineralizing the extract with a boiling concentrated nitric acid sulfuric acid mixture, and reducing aliquots of the mineralized solutions with sodium borohydride. Arsenic can be quantified by emission spectrometry after transfer of the arsine into a dc-helium plasma. Arsenic concentrations of at least 5 ng dm^{-3} of gas can be determined. Application of the hydride generation technique to the non-mineralized extracts indicated that approximately half of the arsenic in the gas is trimethylarsine. Low-temperature GC MS of several gas samples identified trimethylarsine as the predominant arsenic compound in natural gas. Dimethylarsine, methyldiethylarsine, and triethylarsine were also identified in concentrations that decreased with increasing molecular mass of the arsine.

Acknowledgement The financial support of these investigations by the Parker Gas Treating Company, the Robert A Welch Foundation of Houston, Texas, and the Institute of Gas Technology is gratefully acknowledged. The Parker Gas Treating Company and Yates Petroleum Company kindly supplied samples of natural gas.

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